Theoret. chim. Acta (Berl.) 6, 167—185 (1966)

Charge Density Distributions and Sigma Bond Inductive Effects in Hydrocarbons and Hydrocarbon Ions

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Received May 13, 1966

Atomic orbital charge densities have been calculated for the σ electron systems of a number of hydrocarbon molecules, by an electronegativity equalization method. These electron distributions have been used to analyze the relative inductive effects of alkyl groups, the transmission of electronic effects through localized bonds, the inductive stabilization of simple hydrocarbon ions, and the dependence of the ^{1}H and ^{13}C chemical shifts on the corresponding partial charges of the atoms. The charge densities calculated by electronegativity equalization were compared to those predicted by various molecular orbital methods.

Mit Hilfe einer Methode, die auf der Angleichung von Elektronegativitäten beruht („electronegativity equalization"), sind atomare Orbitalladungsdichten für σ-Elektronensysteme einer Reihe von Kohlenwasserstoffmolekülen berechnet worden. Die Ladungsdichten werden mit den Voraussagen verschiedener MO-Methoden verglichen.

Diese Elektronenverteilungen werden zur Analyse der relativen induktiven Effekte von Alkylgruppen, der Weiterleitung elektronischer Effekte durch lokalisierte Bindungen, der induktiven Stabilisierung einfacher Kohlenwasserstoffionen und der Abhängigkeit der chemischen Verschiebung von ^{1}H und ^{13}C von den partiellen Ladungen der Atome benutzt.

Les densités de charge dans les orbitales atomiques ont été calculées pour les systèmes d'électrons σ d'un certain nombre de molécules d'hydrocarbure à l'aide d'une méthode d'égalisation des électronégativités. Ces distributions électroniques ont été utilisées pour analyser les effects inductifs relatifs des groupements alkyles, la transmission des effets électroniques à travers les liaisons localisées, la stabilisation par effet inductif des ions hydrocarbures simples, et la relation entre les déplacements chimiques de ^{1}H et ^{13}C et les charges atomiques partielles correspondantes. Les densités de charges calculées ici ont été comparées à celles obtenues par différentes méthodes d'orbitales moléculaires.

Introduction

In previous reports [*1*, *28*] it was shown that the SGOBE method of orbital electronegativity equalization could be used to estimate charge densities in non-conjugated molecules. The SGOBE method is a localized bond technique which explicitly considers intra-atomic electron repulsions, but neglects the effects of all inter-atomic contributions to the molecular energy. The theoretical foundation of electronegativity equalization methods is discussed in some detail elsewhere [*2*].

In this paper, charge densities calculated by the electronegativity equalization method are reported for a number of hydrocarbons and hydrocarbon ions. The charges were calculated by the SGOBE method previously described [*28*]. The only data required consists of the parameters $\alpha_j, \beta_j, \ldots \zeta_j$ which relate the ionization potential and electron affinity of valence shell atomic orbitals ϕ_j to the total

Table 1. *Energy parameters*[a b]

Atom	Valence State	Atomic Orbitals Included in "n_T"	α_j	β_j	γ_j	δ_j	ε_j	ζ_j
C	$te_j\,te_k\,te_l\,te_m$	$te_k\,te_l\,te_m$	57.067	−17.240	1.029	44.465	−20.880	2.169
C	$tr_j\,tr_k\,tr_l\,\pi_m^1$	$tr_k\,tr_l$	40.853	−14.387	0.886	26.049	−16.226	2.089
C	$tr_j\,tr_k\,tr_l\,\pi_m^0$	$tr_k\,tr_l$	60.373	−19.081	1.482	37.478	−15.126	1.152
C	$di_j\,di_k\,\pi_l^1\,\pi_m^1$	di_k	28.153	−11.282	0.554	12.965	−11.456	1.836
C	$\pi_j\,tr_k\,tr_l\,tr_m$	$tr_k\,tr_l\,tr_m$	56.622	−19.110	1.319	45.392	−22.156	2.345
C	$\pi_j\,\pi_k^1\,di_l\,di_m$	$di_l\,di_m$	38.481	−16.107	1.230	26.161	−17.724	2.348
H	s_j	None	13.60			0.75		

[a] All values of $\alpha_j \rightarrow \zeta_j$ are in eV, and were calculated from the energy data of Ref. [8] according to the method previously outlined [28].

[b] The parameters δ_j, ε_j and ζ_j for C (*tetetete*) are derived for $n_T = 2, 3, 4$ which gives a more accurate fit for the molecules considered, than those previously listed [28] for $n_T = 1, 3, 5$. To the accuracy of the orbital populations given in the previous paper [28] there is no significant difference between the two sets of parameters for E_{vj}.

electron density, N_T, of the other valence shell orbitals of the same atom [28]. The values of $\alpha_j, \beta_j \ldots \zeta_j$ for orbitals of carbon and hydrogen atoms are listed in Tab. 1.

Charge Distributions in Alkanes

The charge distributions in a number of branched and unbranched alkanes have been calculated and are listed in Tab. 2 through 5. Pure te hybridization for the four carbon atom bonding orbitals has been assumed in all cases.

Table 2. *Ionic characters of carbon-hydrogen bonds in the n-alkanes* $C_m H_{2m+2}$

I m	II C_1	III C_2	IV C_3	V C_4	VI C_5
1	1.48				
2	1.79				
3	1.87	2.05			
4	1.89	2.12			
5	1.90	2.14	2.20		
6	1.90	2.15	2.22		
7	1.90	2.15	2.22	2.24	
8	1.90	2.15	2.23	2.25	
9	1.90	2.15	2.23	2.25	2.25
10	1.90	2.15	2.23	2.25	2.25

Numbering scheme for Tab. 2, 4, 5 described in text. All ionic characters represent $C^{\delta-}$ $H^{\delta+}$ and are in percents.

All the hydrogen atoms in the alkanes possess small net positive charges (relative to the neutral atoms), of the order of +0.02 electron; thus i_{CH}, the ionic character of the carbon-hydrogen bonds, is about 2%. Although this net charge is very small, definite variations from molecule to molecule, and within the same molecule, are found in the unbranched *n*-alkanes (Tab. 2). The numbering system in Tab. 2 is such that C–H bonds in the terminal methyl groups are denoted C_1, C–H bonds in the adjoining methylene ($-CH_2-$) unit are denoted C_2, etc.

For each *n*-alkane, the C–H bonds are calculated to become increasingly polar (i.e. the hydrogen atom net charge increases) as the "center" of the molecule is approached. A comparison of i_{CH} values for C_1 between different alkanes (column 2, Tab. 2) indicates increasing polarity of this bond with increasing chain length m. The latter trend illustrates the increase in electronegativity of an unbranched alkyl group with its length. The trend for the C_1–H bonds is general for each position C_2, C_3, etc. For both trends, the magnitude of the effects decreases rapidly with increasing chain length.

The electronegativity of alkyl groups is greater than hydrogen in the alkanes, and successive replacement of the hydrogen atoms in CH_4 by alkyl groups results in increasing polarity to the C–H bonds. The series $Me_{(4-m)}\, CH^*_m$ ($m = 4 \rightarrow 1$) is illustrated in Tab. 3 (column 2); the net positive charge on hydrogen increases

Table 3. *Charge density and* NMR τ *data for hydrogen atoms in branched alkanes* $(CH_3)_{4-m}\, CH_m$

I Molecule	II H* Hydrogen Charge Density	III NMR τ for H* Protons	IV "Methyl" Hydrogen Charge Density	V NMR τ for "Methyl" Protons
CH_4^*	0.985_2	9.774	—	—
$CH_3CH_3^*$	0.982_1	9.144	0.982_1	9.144
$(CH_3)_2CH_2^*$	0.979_5	8.657	0.981_3	9.094
$(CH_3)_3CH^*$	0.977_3	8.260	0.980_6	9.110
$(CH_3)_4C$	—	—	0.980_0	9.073

All NMR τ data is from Ref. [17], for CCl_4 solutions of the alkanes.

with increasing methyl substitution (decreasing m). This trend of C–H bond polarity for primary, secondary and tertiary carbon atoms is identical to that found in earlier electronegativity calculations by FERREIRA [5]. A molecular orbital calculation on propane by SANDORFY [23] predicted a greater net positive charge on the methylene hydrogen compared to the methyl, in agreement with the general trend noted above, and the present results for propane (Tab. 3, row 3). In the extended Hückel theory of HOFFMANN [11, 12], the magnitude of, and variations in, the hydrogen atom net charges generally conflict with the n-alkane trends in Tab. 2.

POPLE and SEGAL have recently introduced an SCF–LCAO–MO scheme [21] which assumed complete neglect of differential overlap. The magnitude of the hydrogen atom net charges for methane and ethane is in good agreement with the present work, but the change in the H net charge from methane to ethane (+0.0354 to +0.0334), is in the opposite direction to the equalization results (+0.0148 to +0.0179).

Proton NMR data for the hydrogen atoms in the series $(CH_3)_{4-m}\,CH_m$ are listed in Tab. 3 along with the calculated hydrogen atom charge densities n_H. The local diamagnetic shielding σ_{LD} at a proton is a function of the electron density surrounding that proton, and can be approximately expressed as [22]

$$\sigma_{LD} = K n_H \qquad K = 20 \times 10^{-6}\,.$$

The exact value, theoretically derived, for K is dependent upon the effective nuclear charge chosen for hydrogen [22]. Since local paramagnetic effects for hydrogen are small [22], a linear correlation between the experimentally determined shielding of the proton (expressed in terms of τ) and the calculated hydrogen atom charge densities n_H is expected. Such a relationship has been established for the chloroalkanes [13] by use of electronegativity equalization charge densities [28].

In Fig. 1 the proton NMR τ values have been plotted against the hydrogen atom charge densities for the series $(CH_3)_{4-m}\,CH_m$. Two separate lines, of radically different slope, are produced; one for the H* in $(CH_3)_{4-m}\,CH_m^*$ (curve A), the other for the "methyl" hydrogens (curve B).

The slope of curve A, about 190 ppm per electron, is much greater than the theoretical value of about 20, although the sign of the slope is correct. The large slope of curve A may be due to either an underestimation of the magnitude of the charge density changes in this series by the equalization calculation method, or by changes in the proton shieldings due to neighbour anisotropy effects. The latter effects have been estimated for this series [17] and would produce τ variations for the protons concerned, in the same direction as the charge density effects (increasing shielding with increasing m). The hypothesis that both charge density and neighbour anisotropy effects are operative in producing the large slope in curve A is substantiated by the correlation in curve B. For the hydrogen atoms of curve B ("methyl" hydrogens in $(CH_3)_{4-m}\,CH_m$ changes in the neighbour anisotropy shielding contribution are much smaller [17], and the slope of the correlation line ($\simeq$ 27 ppm per electron) is much closer to the theoretical value.

The carbon-carbon bond polarities, i_{CC}, are exceedingly small (0.0 to 0.6%) in the n-alkanes. Nevertheless the variations in i_{CC} show certain regularities (Tab. 4). In every n-alkane, the absolute magnitude of i_{CC} decreases as the distance from

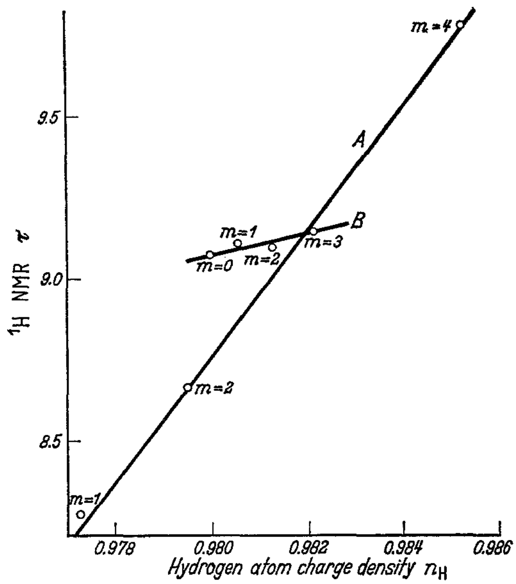

Fig. 1. Plot of calculated Hydrogen atom net charge density against ¹H N.M.R. τ value for the methylated methanes $(CH_3)_{4-m}\,CH_m^*$

Curve *A* represents the H* hydrogen atoms, curve *B* the "methyl" hydrogens. Data from Tab. 3.

the chain end increases, and the polarities of the C–C bonds show that the carbon atom nearest the end of the chain always forms the positive end of the carbon-carbon linkage. In *n*-hexane ($m = 6$) for example, the first "methylene" carbon atom (C_2) forms the negative end of the $C_1 - C_2$ bond which has an ionic character of 0.55%, while C_2 is the positive end of the $C_2 - C_3$ link where $i_{CC} = 0.15\%$. The polarity of a given C – C bond, for example that between C_1 and C_2, (data for which is given in Column 2 of Tab. 4) generally increases as the chain length (m) increases.

All three trends in the i_{CC} values are in accord with the observation that the electronegativity of an alkyl group in the unsubstituted alkanes increases with length.

Table 4. *Ionic characters of carbon-carbon bonds in the n-alkanes* $C_m\,H_{2m+2}$

I m	II C_1–C_2	III C_2–C_3	IV C_3–C_4	V C_4–C_5
2	0.00			
3	0.40			
4	0.51	0.00		
5	0.54	0.11		
6	0.55	0.15	0.00	
7	0.55	0.16	0.03	
8	0.55	0.16	0.04	0.00
9	0.55	0.16	0.05	0.01
10	0.55	0.16	0.05	0.01

Ionic characters in percents. C–C bond polarities are such that carbon nearest middle of molecule is δ–.

In all the neutral alkanes, the electronegativity order

$$\chi^{(1)}_{\text{tertiary C}} > \chi^{(1)}_{\text{secondary C}} > \chi^{(1)}_{\text{primary C}} > \chi^{(1)}_{\text{C in CH}_3} > \chi^{(1)}_{\text{H}}$$

is found, and consequently the direction of charge transfer may be predicted without calculation for most localized bonds in this series. For example, in methylcyclohexane the ring carbon attached to the methyl group forms the negative end of the ring carbon-methyl carbon linkage since $\chi^{(1)}_{\text{tertiary C}} > \chi^{(1)}_{\text{C in CH}_3-}$; the ring carbon attached to $-CH_3$ is however the negative end of the bonds to adjacent ring carbons. All the carbon-hydrogen bonds are polar in the sense $C^{\delta-}-H^{\delta+}$.

The ionic character data for the C–H bonds (Tab. 2) and the C–C bonds (Tab. 4) in the *n*-alkanes may be combined to calculate the total charge densities and net atomic charges (deviation from neutral atoms) of the carbon atoms. The net atomic charges are collected in Tab. 5.

Table 5. *Carbon atom net charges in the n-alkanes* $C_m H_{2m+2}$

I m	II C_1	III C_2	IV C_3	V C_4	VI C_5
1	−0.0591				
2	−0.0536				
3	−0.0521	−0.0489			
4	−0.0517	−0.0475			
5	−0.0516	−0.0472	−0.0462		
6	−0.0515	−0.0470	−0.0458		
7	−0.0515	−0.0470	−0.0457	−0.0455	
8	−0.0515	−0.0470	−0.0457	−0.0453	
9	−0.0515	−0.0470	−0.0457	−0.0453	−0.0452
10	−0.0515	−0.0470	−0.0457	−0.0453	−0.0452

All the carbon atoms in the *n*-alkanes are found to bear small net negative charges, of the order −0.05 electron. The net charge of a carbon atom in a definite position (e.g. C_1, listed in column 2, Tab. 5) decreases as the chain length is increased, again the result of the dependence of alkyl radical electronegativity on length.

Within a single *n*-alkane molecule, the net negative charges of the carbon atoms decrease as the number of C–C bonds between the carbon concerned and the chain end increases. This trend is the net result of two opposing effects; (I) the increasing charge transfer from the hydrogens to the carbons as the center of the chain is approached, and (II) the decreasing transfer of electron density from the adjoining carbon atoms (through i_{CC}) towards the center. Since the changes in i_{CC} with position are greater than the changes in i_{CH}, the second effect predominates and causes the decrease in net charge as the center of the molecule is approached.

Using the extended Hückel method, HOFFMANN [*11*] has calculated the carbon net atomic charges for the *n*-alkanes. The net charges are all negative as in the present results, but the magnitudes of the charges are generally much greater than those in Tab. 5. In both calculation methods the terminal methyl carbons are predicted to be the most negative, but there is no general agreement in the other carbon net charge trends. An analysis of the charge distributions predicted by the extended Hückel theory is presented elsewhere [*24*].

On the basis of empirical observations [*26*], and theoretical considerations [*16*, *20*, *22*], carbon atom net charges are expected to correlate with ^{13}C N.M.R. chemical shifts. The chemical shift $\delta_{C_{(A)}}$ of carbon A may be expressed as

$$\delta_{C_{(A)}} = K_1 + K_2\, q_{C_{(A)}} \,.$$

The proportionality factor K_2 has been empirically estimated to be 160 to 200 ppm per electron [*26*]. Correlation of $\delta_{C_{(A)}}$ and electronegativity equalization carbon charges $q_{C_{(A)}}$ for the chloromethanes required $K_2 \simeq 290$ [*28*].

Grant and Paul [*7*] have measured the chemical shifts of each carbon atom in a series of *n*-alkanes and several branched alkanes. All the ^{13}C chemical shift data discussed herein is from Tab. 1 of their paper [*7*], and is relative to benzene for which $\delta_C = 0$. An empirical analysis of the ^{13}C chemical shift data for the *n*-alkanes indicated that $\delta_{C_{(k)}}$ for any carbon k in this series could be accurately fixed by the relationship [*7*]

$$\delta_{C_{(k)}} = B + \sum_m A_m N_{k_m}$$

where B is a constant approximately equal to the chemical shift in methane, N_{k_m} is the number of carbon atoms in the m^{th} position relative to carbon k, and A_m is a chemical shift parameter for the m^{th} carbon atom. From the A_m parameters listed by Grant and Paul (their Tab. 2), a parameter D can be calculated for each *n*-alkyl group [*19*]. The group parameters D are linearly related to the SGOBE electronegativities $\chi^{(1)}$ for the group (evaluated assuming the radical's bonding AO is a singly-occupied tetrahedral hybrid) as shown in Fig. 2, with the exception of D corresponding to the ethyl group.

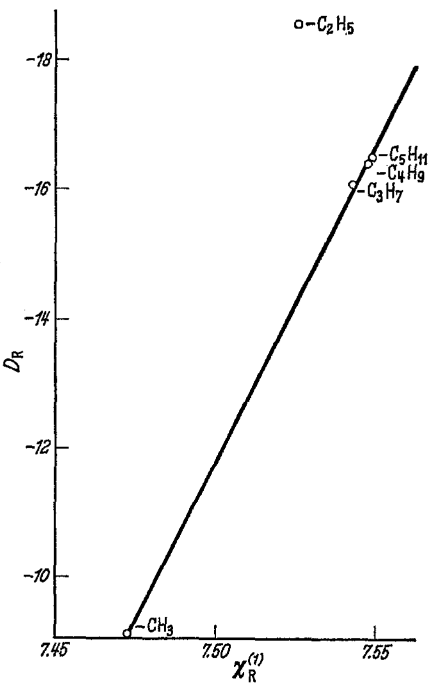

Fig. 2. Plot of alkyl radical electronegativity χ^1_R against the empirical ^{13}C NMR chemical shift parameter D_{R}..

The trends in ^{13}C chemical shifts $\delta_{C_{(A)}}$ for the *n*-alkanes correlate qualitatively with the carbon atom net charge variations (Tab. 5). Within a given unbranched alkane, $\delta_{C_{(A)}}$ and $|\, q_{C_{(A)}} |$ both decrease as the number of C–C bonds between carbon A and the end of the molecule increases. The difference in both $\delta_{C_{(A)}}$ and $q_{C_{(A)}}$ between successive carbon atoms in the chain decreases as the center of the molecule is approached. For a carbon atom of given position (e.g. C_1), δ_C and $|\, q_C |$ both decrease with increasing chain length, and the changes between successive *n*-alkanes fall rapidly as the chain is lengthened. Deviations from the parallel variations of $\delta_{C_{(A)}}$ and $|\, q_{C_{(A)}} |$ always arise when carbon A is attached to one or more ethyl groups (e.g. terminal carbon in propane).

The ^{13}C N.M.R. chemical shifts $\delta_{C_{(A)}}$ for the *n*-alkanes are plotted against the

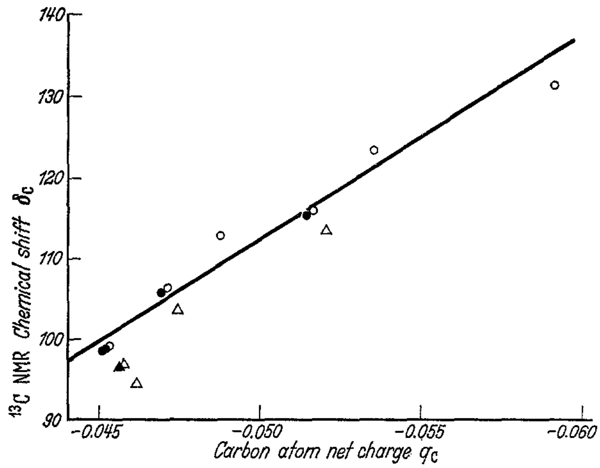

Fig. 3. Plot of the Carbon atom net charges against the corresponding ^{13}C NMR chemical shifts for the *n*-alkanes CH_4 through $C_{10}H_{22}$

The filled in points represent several different carbon atoms having almost the same q_C and δ_C. The triangles represent carbon atoms directly bonded to ethyl groups, the circles represent all other carbon atoms. The ^{13}C NMR data is from Ref. [7]; δ_C is relative to that of benzene

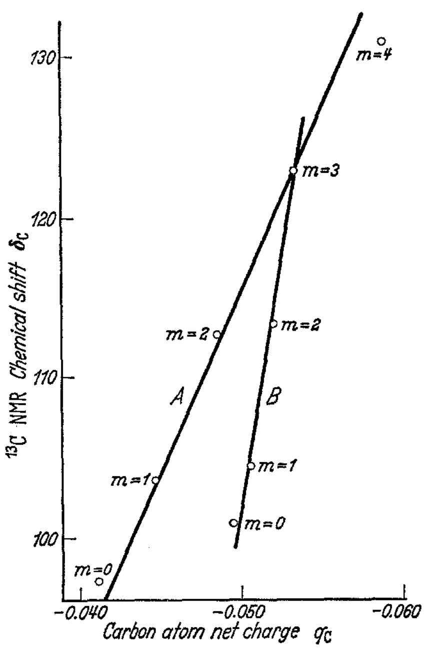

Fig. 4. Plot of the Carbon atom net charges against the ^{13}C NMR chemical shifts in the methylated methane series $(CH_3)_{4-m}C^*H_m$.

Curve *A* represents the C* carbon atoms, curve *B* the "methyl" carbons. All chemical shifts are relative to benzene and are from Ref. [7]

calculated carbon atom net charges (Tab. 5) in Fig. 3*. The slope of the best straight line in this correlation is about 2800 ppm per electron, and is of the correct sign but about fifteen times as large as expected.

The correlation of $\delta_{C(A)}$ with $q_{C(A)}$ for the carbon atoms of the methylated methane series $(CH_3)_{4-m}\,CH_m$ is given in Fig. 4. As for the proton shift correlations in this series (Fig. 1), two straight lines are evident, one for the central carbons (curve A) of slope −1700 ppm per electron, and one for the methyl group carbons (curve B) of slope −6500 ppm per electron.

In general, the ^{13}C chemical shifts correlate reasonably well with the calculated carbon net charges for particular series within the alkanes, but the chemical shift-charge density proportionality constant, K_2, differs for each series and ranges from 10 to 35 times the established value.

Grant and Paul [7] established a direct linear proportionality between the n-alkane ^{13}C chemical shifts parameters and the nuclear screening effects due to the anisotropy ΔX^{CC} of the carbon-carbon single bonds. The value of ΔX^{CC} required to quantitatively account for the large range ($\simeq$ 40 ppm) of $\delta_{C(A)}$ in the n-alkanes is however about two orders of magnitude greater than previously calculated values.

Both SGOBE charge density and C–C bond anisotropy changes are therefore capable of qualitatively accounting for the chemical shifts of the alkanes, but neither contribution alone (nor their sum) can quantitatively account for the wide range of chemical shifts observed. Part of the difficulty in the charge density correlations may be due to an inherent underestimation of the ionic characters of, and changes in the ionic characters of, carbon-carbon and carbon-hydrogen bonds determined by using an electronegativity equalization method [2, 10]. It seems unlikely, however, that this factor is totally responsible for the wide range of chemical shifts observed.

Sigma Bonds in Unsaturated Hydrocarbons

Since the electronegativity of a singly-occupied carbon s-p hybrid atomic orbital increases linearly with the extent of s orbital character [8], in general for the σ bonds

$$\chi^{(1)}_{\text{digonal C}} > \chi^{(1)}_{\text{trigonal C}} > \chi^{(1)}_{\text{tetrahedral C}} \,.$$

The replacement of a carbon-carbon single bond ($C_{te} - C_{te}$) in an alkane by either a double or triple carbon-carbon bond will therefore result in charge density shifts toward the unsaturated bond from the rest of the alkane.

Charge density data for several symmetric unsaturated hydrocarbons is listed in Tab. 6. Pure (sp^2) hybridization was assumed for each σ bond of the unsaturated carbon atoms in the ethylenes and benzenes, pure (sp) hybridization for the σ bonds of an acetylenic carbon. Only symmetric molecules in which the π-atomic-orbitals are singly-occupied were considered, due to the difficulties in SGOBE calculations for π-bonds [2, 28].

The carbon-hydrogen bond polarities in the sequence ethane, ethylene, and acetylene increase with the s orbital character of the carbon orbital bonded to

* The points for carbon atoms bonded to ethyl groups deviate most from the line, and are represented as triangles rather than circles.

Table 6. *Calculated charge density and energy data for some unsaturated hydrocarbons*

Molecule	i_{CH} of C_{tr}–H Bond	i_{CC} of C_{tr}–C_{te} Bond	i_{CH} of C_{te}–H Bond	Unsaturated Carbon Atom Net Charge	I_{V_π} (in eV)	E_{V_π} (in eV)	h_C with β_{CC} = −1 eV	h_C with β_{CC} = −4 eV
$H_2C=CH_2$	4.52	—	—	−0.0904	10.162	−0.686	−0.28	-0.06_9
MeHC=CHMe	4.60	4.28	2.68	−0.0888	10.179	−0.674	−0.26	-0.06_6
$Me_2C=CMe_2$	—	4.38	2.70	−0.0875	10.193	−0.664	−0.25	-0.06_3
EtHC=CHEt	4.69	4.03	2.88 (*a*) 2.13 (*b*)	−0.0872	10.197	−0.662	−0.25	-0.06_2
Benzene	6.08	—	—	−0.0608	10.487	−0.457	−0.00	-0.00_0
Hexamethyl-benzene	—	6.31	3.10	−0.0631	10.462	−0.475	−0.02	-0.00_5

Molecule	i_{CH} of C_{di}–H Bond	i_{CC} of C_{di}–C_{te} Bond	i_{CH} of C_{te}–H Bond	Unsaturated Carbon Atom Net Charge	I_{V_π} (in eV)	E_{V_π} (in eV)	h_C with β_{CC} = −1 eV	h_C with β_{CC} = −4 eV
HC≡CH	11.92	—	—	−0.1192	9.871	−0.855	−0.51	-0.12_7
MeC≡CMe	—	13.78	4.67	−0.1378	9.669	−0.988	−0.67	-0.16_9
EtC≡CEt	—	13.73	4.72 (*a*) 2.71 (*b*)	−0.1373	9.674	−0.995	−0.67	-0.16_9

In column 4, (*a*) represents "methylene" C–H bonds, and (*b*) "methyl" C–H bonds. All i_{CH} are in the sense $C^{\delta-}$–$H^{\delta+}$. All i_{CC} represent bonds in which the charge transfer is toward the unsaturated carbon atom.

hydrogen, in agreement with the experimental order of hydrogen atom acidity for the series [3]. The hydrogen net charges (+0.018, +0.045, +0.119 respectively) are in fair agreement with those calculated by POPLE and SEGAL's CNDO method (+0.033, +0.046, +0.107 respectively) [21].

Successive replacement of the hydrogen atoms in $CH_2 = CH_2$ by methyl groups leads to a decrease in the unsaturated carbon atom's net negative charge (Tab. 6, column 5) since the $C_{te} - C_{tr}$ bonds are not as ionic as the H–C_{tr} bonds (Tab. 6, columns 3 and 2). Total replacement of the hydrogen atoms by methyl groups in benzene, on the other hand, leads to a higher net negative charge on the unsaturated carbon, since the $C_{te} - C_{tr}$ bonds are more ionic here than the H–C_{tr} bonds. Alkyl groups are therefore predicted by the electronegativity equalization calculations to be electron-releasing relative to hydrogen in benzenes, but electron withdrawing in the ethylenes. The net effects of alkyl substitution are small in both series, and the reversal of direction of charge density transfer is due to an increase in the self-consistent $\chi_{tr}^{(1)}$ value in the benzene series compared to the ethylenes (see next section).

Replacement of the hydrogen atoms by methyl groups in acetylene leads to a substantial increase in the digonal carbon atom's net charge, due to the greater polarity of a C_{te}–C_{di} bond (about 13.8%) compared to that of H–C_{di} (about 11.9%).

The carbon-hydrogen bonds associated with the substituted methyl and ethyl groups in the ethylene, benzene and acetylene series are all more polar (Tab. 6, column 4) than in the alkanes due to the transmission of the unsaturated carbon atom inductive effect through the C–C bonds.

In the sixth and seventh columns of Tab. 6, the effects of the σ bond framework electronic charge density upon the ionization potential and electron affinity (I_{V_π}, E_{V_π}) of the singly-occupied π-bonding atomic orbitals are listed. Both parameters are significantly smaller in the acetylenes than in the ethylenes and benzenes, although the effect of methyl substitution for hydrogen at the unsaturated carbon atoms within each series (acetylenes, benzenes, ethylenes) is very small. The change in "Mulliken" electronegativity of a singly-occupied π atomic orbital

$$\chi_\pi^{(1)} = \tfrac{1}{2}\,(I_{V_\pi} + E_{V_\pi})$$

upon substitution of one H–C_{tr} bond by H_3C–C_{tr} is then about +0.01 ev in the ethylenes and −0.02 ev in the benzenes. Now owing to the direct correspondence between $\chi_\pi^{(1)}$ and the Hückel LCAO-MO π-system parameter α_C for a carbon atom [2, 18]

$$\alpha_C = -\chi_\pi^{(1)}$$

the α_C for various σ bond frameworks may be estimated. α_C is normally expressed as [27]

$$\alpha_C = \alpha_0 + h_C\,\beta_0$$

$$h_C = \frac{\chi_0^{(1)} - \chi_\pi^{(1)}}{\beta_0}$$

where α_0, β_0, $\chi_0^{(1)}$ are the Hückel coulomb and resonance integrals and the electronegativity in the benzene π electron system. Estimates of β_0 vary widely, and for this reason the parameters h_C have been calculated for $\beta_0 = -1$ ev, and $\beta_0 = -4$ ev. The values h_C for the unsaturated carbon atoms are listed in columns 8 and 9 of Tab. 6. Substantial variations in h_C between the three series (ethylenes, benzenes, acetylenes) are found, although within each series the effect of alkyl substitution is quite small. Empirical estimates of the change in h_C for benzene upon substitution of hydrogen by methyl groups are in the range 0.0 to $-0.1\,\beta_0$ ("conjugation model" [27]) compared to the change of about $-0.01\,\beta$ from the present results. In ethylene, methyl substitution for hydrogen leads to a change in h_C of about the same magnitude, but opposite sign (Tab. 6).

Variations in Group Electronegativities

In preceding sections, it has been noted that the sign and magnitude of the alkyl group inductive effect, relative to that of hydrogen, is dependent upon the molecular environment. This effect will be discussed further in this section by analyzing the variations in group electronegativity which occur when a group (such as methyl) is present in different molecules. The discussion will center around $\chi_j^{(1)}$, the "Mulliken" electronegativity of a group with bonding atomic orbital ϕ_j, and its dependence upon n_j, the orbital charge density of ϕ_j, in some bond between ϕ_j and another orbital ϕ_k. Note that the behavior of $\chi_j^{(1)}$ will be discussed, not that of the so-called bond electronegativity function $\chi_j(n_j)$ [2, 9, 28]; the ionic character of the $j-k$ bond is a direct function of $\chi_j^{(1)}$ and $\chi_k^{(1)}$.

For the bonding orbital of a monovalent atom, $\chi_j^{(1)}$ is not a function of n_j, since for a given hybrid atomic orbital ϕ_j, I_{Vj} and E_{Vj} are not dependent upon n_j (under the SGOBE approximations). If ϕ_j is a bonding orbital of a polyvalent atom, however, I_{Vj} and E_{Vj} are dependent upon the total charge density n_T of the atomic orbitals of same atom as ϕ_j, and this density n_T is in turn dependent upon n_j. The Mulliken electronegativity $\chi_j^{(1)}$ of a group bonding orbital ϕ_j will then be dependent on n_j, that is $\chi_j^{(1)}$ will vary with molecular environment.

Consider a group R_3C– bonded to an identical group $-CR_3$; in this case $n_j = 1$ in the bond between the two groups. If instead R_3C– is bonded to a group $-CR'_3$ of higher electronegativity, then $n_j < 1$. The decrease in n_j in $R_3C{-}CR'_3$ compared to $R_3C{-}CR_3$ will induce electronic charge density to flow towards C in each R–C bond, thereby decreasing I_{Vj}, E_{Vj} and hence $\chi_j^{(1)}$. (See Figs. 1 and 2 of reference [28]).

If $-CR'_3$ is a group whose electronegativity is lower rather than higher than that of R_3C–, then $n_j > 1$, and this increase in n_j will induce a transfer of electron density away from C in each R–C bond. This decrease in electron density in the atomic orbitals of C (except for ϕ_j) will then increase I_{Vj}, E_{Vj} and $\chi_j^{(1)}$.

The electronegativity $\chi_j^{(1)}$ of a group is therefore, not expected to be a constant, but to vary with the nature of the complementary group to which it is attached. From the qualitative considerations of the molecules $R_3C{-}CR'_3$ above, $\chi_j^{(1)}$ is expected,

1. to increase smoothly as n_j increases, and

2. to decrease as the electronegativity of the complementary group increases.

Effects 1 and 2 are graphically illustrated in Figs. 5 and 6 respectively.

For low values of n_j (highly electronegative complementary groups), the lines of Fig. 5 indicate that

$$\chi_{\mathrm{H}}^{(1)} > \chi_{-\mathrm{CH_3}}^{(1)} > \chi_{-\mathrm{CH_2Me}}^{(1)} > \chi_{-\mathrm{CHMe_2}}^{(1)} > \chi_{-\mathrm{CMe_3}}^{(1)}$$

which is the "normal" inductive order-that is, methyl groups "feed in" electron density relative to hydrogen. With high n_j (complementary groups of low electronegativity), however, the order given above is exactly reversed, and substitution of hydrogen by a methyl group leads to a withdrawal of charge density.

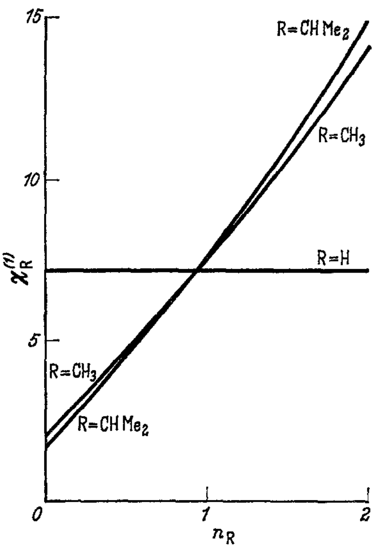

Fig. 5

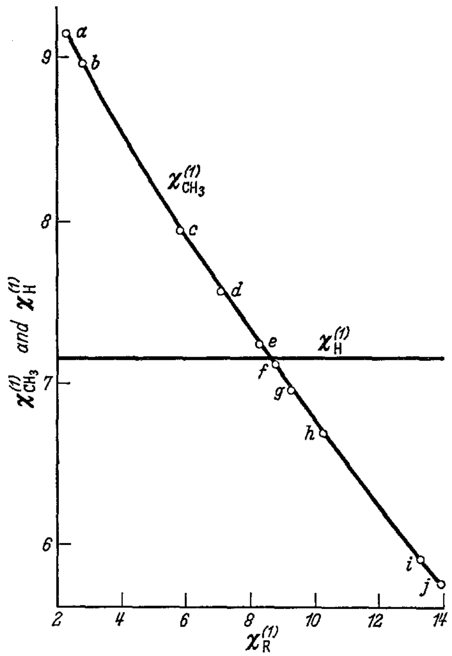

Fig. 6

Fig. 5. Plot of the electronegativity $\chi_R^{(1)}$ of several groups R against the orbital charge density n_R

The curve for $-CH_2Me$ lies between that of $-CH_3$ and $-CHMe_2$. The curve for $-CMe_3$ lies to the side of the $-CHMe_2$ curve opposite to that of $-CH_3$. All the alkyl group curves cross at approximately the same point, slightly before they cross the line for $-H$

Fig. 6. Plot of $\chi_{\mathrm{CH_3}}^{(1)}$ and $\chi_{\mathrm{H}}^{(1)}$ against $\chi_{\mathrm{R}}^{(1)}$ for the molecules $R\text{-}CH_3$ and R-H

Legend for groups R: a) $-CH_2^-$; b) $-CHMe^-$; c) $-CH_2CH_2^-$; d) $-H$; e) $-CH=CHMe$; f) $-C_6Me_5$; g) $-CH_2CH_2^+$; h) $-C\equiv CMe$; i) $-CHMe+$; j) $-CH_2^+$

In Fig. 6, the Mulliken electronegativities of the methyl group and the hydrogen atom have been plotted as a function of the complementary group R's electronegativity $\chi_{\mathrm{R}}^{(1)}$ in the species $R\text{–}CH_3$ and R–H. For low $\chi_{\mathrm{R}}^{(1)}$ (e.g. R corresponding to alkyl groups in the alkanes) $\chi_{-\mathrm{CH_3}}^{(1)} > \chi_{\mathrm{H}}^{(1)}$ and the replacement of hydrogen by a methyl group leads to a withdrawal of electron density from R. If $\chi_{\mathrm{R}}^{(1)}$ is very high, however, (R corresponding to an acetylenic carbon, or an alkyl group with positive charge), $\chi_{\mathrm{H}}^{(1)} > \chi_{-\mathrm{CH_3}}^{(1)}$ and the methyl group becomes a more effective electron donor than hydrogen. Note particularly the points *e* and *f* (Fig. 6) which correspond to -CH = CHMe and the pentamethylphenyl radicals respectively. In the former case (point *e*), $\chi^{(1)}_{-CH_3}$ is a little greater than $\chi^{(1)}_{H}$, in the latter case $\chi^{(1)}_{-CH_3}$ is a little less than $\chi^{(1)}_{H}$. This change of order between the two electronegativities around the point corresponding to a complementary group whose first atom is a trigonal carbon accounts for the anomolous inductive effects encountered in the ethylenes and benzenes (see previous section).

Analysis of the SGOBE charge densities and $\chi^{(1)}_{j}$ values therefore indicates that, unlike a monovalent atom, a group does not possess a constant Mulliken electronegativity value. By use of a different electronegativity equalization method, HUHEEY [14] has also reached this same conclusion.

Transmission of Inductive Effects

In this section the transmission of inductive effects through localized carbon-carbon bonds of hydrocarbon chains and rings will be analyzed. Due to the nature of the approximations implicit in the electronegativity equalization method, no "field effects" (inductive effects transmitted directly through space rather than the carbon-carbon bonds [6]) are included in the results to be discussed. The analysis considers a neutral hydrocarbon which has had one neutral hydrogen atom abstracted from it to produce a "free radical". The orbital charge densities in such a species are compared to the densities in the corresponding positive ion in which a hydride ion (H^-) has been removed from the neutral hydrocarbon. The two species are then equivalent except for the orbital charge density in one bonding atomic orbital, ϕ_j' which has a density of 1 electron in the radical, and 0 electrons in the positive ion. For simplicity, no rehybridization of the atomic orbitals of atom 1 (the atom having orbital ϕ_j) is considered. The remainder of the carbon atoms in the chain (or ring) are numbered such that carbon 2 is directly bonded to 1, carbon 3 directly bonded to carbon 2, etc.

A quantity Δ^H_m may now be defined for each chemically inequivalent hydrogen atom in the system, the parameter m referring to the number of the carbon atom to which the hydrogen atom is directly bonded. Δ^H_m is then defined as the ratio of the change in the hydrogen atom electron density in going from the free radical to the positive ion to the hydrogen atom electron density in the free radical. The various values of Δ^H_m for a given hydrocarbon chain (or ring) then represent the extent to which the electron density at each hydrogen atom is altered when a change of electron density of one electron is made in ϕ_j. Values of Δ^H_1, Δ^H_2, etc. for alkane chains of length 1 to 5 carbon atoms, and for cyclohexane are listed in columns 2 to 6 of Tab. 7. In each case the Δ values represent a decrease in the total charge density at a hydrogen atom in going from the free radical to the positive ion species.

The general trend of Δ^H_m within a chain is a continuous decrease as the number of carbon-carbon bonds between C_1 and C_m increases. For example the Δ^H_m values for chain length of 5 decrease smoothly from $\Delta^H_1 = 0.192$ to $\Delta^H_5 = 0.002$. These decreases correspond to a damping along the chain of the inductive effect produced at C_1.

The ratios $\frac{\Delta^H_m}{\Delta^H_{(m-1)}}$ within each chain are listed in columns 7 to 10 of Tab. 7. These ratios for hydrocarbon chains appear to be generally independent of chain length and position. The general value of this ratio will be defined as k, the transmission coefficient of the inductive effect. For m corresponding to a "methylene" ($-CH_2-$) unit, $k = 0.300 \pm 0.007$, while for terminal methyl groups ($-CH_3$), $k = 0.320 \pm 0.008$. These transmission coefficients compare quite well with $k = 0.36$, found experimentally from a study of substituent effects on the acidity of carboxylic acids [*27*]. The magnitudes of the k values, and the existence of different k for methylene and methyl units, are in excellent accord with those determined (0.29 for $-CH_2-$, 0.34 for $-CH_3$) from the empirical charge distribution calculation method of Smith and Eyring [*25*].

The Δ_m^H for a given position m is found to decrease as the chain length is increased, and in each case Δ_m^H converges toward a constant value. The decrease in Δ_m^H with length is due to the increased number of atoms over which the positive charge induced at C_1 can be spread.

Quantities Δ_m^C may be defined as the ratio of the change in total carbon atom electron density (from radical to positive ion) to the carbon density in the radical. The Δ_m^C values are not listed since, for all systems considered, the ratios $\Delta_m^C/\Delta_{(m-1)}^C$ are identical (within limits ± 0.01) to the corresponding $\Delta_m^H/\Delta_{(m-1)}^H$ values for the equivalent positions.

The relative invariance of k for methylene carbon units within the same chain indicates that k is independent of the magnitude of the inductive effect being transmitted through the unit, since the size of this effect does vary considerably from atom to atom within each chain; there is only a very slight trend of k increasing with increasing size of the inductive effect. (E.g. Δ_2/Δ_1 is generally about 0.01 greater than Δ_3/Δ_2).

In the cyclohexane system (row 6 of Tab. 7), the Δ_m^H trends are similar to those established above for the alkane chains. The (Δ_4^H/Δ_3^H) ratio is abnormally

Table 7. *Inductive effect transmission data for hydrocarbon chains and rings*

I Length of *n*-alkane chain or molecule name	II Δ_1^H	III Δ_2^H	IV Δ_3^H	V Δ_4^H	VI Δ_5^H	VII Δ_2^H/Δ_1^H	VIII Δ_3^H/Δ_2^H	IX Δ_4^H/Δ_3^H	X Δ_5^H/Δ_4^H
1	0.217								
2	0.194	0.064				0.32_8			
3	0.192	0.059	0.017			0.30_6	0.31_6		
4	0.192	0.058	0.017	0.005		0.30_5	0.29_5	0.31_4	
5	0.192	0.058	0.017	0.005	0.002	0.30_4	0.29_4	0.29_4	0.31_3
Cyclohexane	0.173	0.053	0.017	0.009		0.30_4	0.31_6	0.53_8	
Benzene	—	0.079	0.028	0.016		—	0.35_2	0.58_3	

Δ_m^H are defined in text. Δ ratios calculated from accurate data given to three decimal places under individual Δ headings.

high, as is the corresponding Δ_4^C/Δ_3^C value (both are 0.54). In general all the ratios for monocyclic ring systems are expected to display anomalies of this type, because there exist two bonded pathways, one "clockwise" and the other "anticlockwise", for the inductive effect of substitution to be transmitted from C_1 to any other position C_m. If the inductive effect produced at C_1 is assumed to be transmitted independently in each direction according to the equation $\frac{\Delta_m}{\Delta_{(m-1)}} = k$, the sum of the two independent effects at C_2 will be $k\,(1 + k^4)\,\Delta_1$, at C_3 $k^2\,(1 + k^2)\Delta_1$, and at C_4 $2\,k^3\,\Delta_1$.

Hence

$$\frac{\Delta_2}{\Delta_1} = k\,(1 + k^4), \frac{\Delta_3}{\Delta_2} = k\left(\frac{1+k^2}{1+k^4}\right), \quad \frac{\Delta_4}{\Delta_3} = k\left(\frac{2}{1+k^2}\right)$$

rather than simply k as in the case of the chains. Assuming $k = 0.3$, the three ratios are 0.30, 0.32 and 0.55 respectively, in good accord with the values in Tab. 7. The inductive effects in a monocyclic ring system can then reasonably be considered as an additive combination of two independent effects transmitted from both directions according to the damping factor found for the unbranched chains.

Application of this conclusion to the Δ_m^H ratios for benzene (row 7, Tab. 7. leads to a transmission coefficient k through a trigonal carbon (–CH–) unit of 0.34) This greater k for trigonal compared to tetrahedral carbon atoms is in accord with a statistical analysis of experimental results by BOWDEN [4], although in the present case part of the increase in k may arise from the imposed condition that the π-bonding carbon p orbitals have unit electron charge density in both the radical and positive ion.

Although the calculated transmission of inductive effects through the bonds considered in this section agrees quite well with experimental studies of this effect (carboxylic acid acidity data [27]), it is not possible to establish here whether or not "field effects" are important in these chain and ring systems. The latter effects are expected to display the same type of transmission properties with increasing distance as the "bonded" effects.

Inductive Stabilization of Hydrocarbon Ion

The stability order of carbonium ions generally decreases according to the "nature" of the central carbon atom

$$\text{tertiary} > \text{secondary} > \text{primary}\,.$$

Consider a trigonally hybridized carbon atom, bonded by (sp^2) orbitals to three alkyl groups or hydrogen atoms R_1, R_2, R_3, and having its p_π orbital with a charge density of zero. The formal unit positive charge (due to the vacant p_π orbital) of the carbon atom may be considered to be delocalized from the central carbon to the groups R_1, R_2, R_3 in two ways:

1. *Hyperconjugation* — The vacant p_π orbital may conjugate with atomic orbitals (or group orbitals) of R_1, R_2, R_3 when possible, effectively delocalizing the positive charge by a "π" electron system.

2. *Inductive Stabilization* — By charge transfer in the three R–C_{tr} σ bonds which affects a net decrease in the net positive charge of the trigonal carbon atom, although the p_π atomic orbital remains vacant.

In the present discussion, only effect (2) is considered. The p_π atomic orbital of the central carbon is assumed to be vacant, and the charge distribution in the C–R bonds (and the other bonds within R) are calculated by equalization of the electronegativities. The net positive charges of the trigonal carbon atom in a series of planar carbonium ions $(R_1 R_2 R_3 C)^+$ are listed in column 4 of Tab. 8. The corresponding net charges of the central carbon (for the same series) for $(R_1 R_2 R_3 C)^+$ when C is a tetrahedrally (sp^3) hybridized carbon are listed in the sixth column for comparison. In the latter cases, one (sp^3) atomic orbital, rather than a p_π, is assumed to be vacant.

The electronegativity of the central carbon atom's (sp^2) or (sp^3) orbitals is very high in these cases, due to the vacant p_π or (sp^3) orbital. In such situations, $\chi_H^{(1)} \gg \chi_{CH_3}^{(1)}$ (see Fig. 6), and successive replacement of the hydrogen atoms in $(CH_3)^+$ by methyl groups leads to increasingly lower net positive charge on the central carbon (compare $(CH_3)^+$ with $(CMe_3)^+$).

Table 8. *Carbon and hydrogen atom net charges in the hydrocarbon ions* $(R_1R_2R_3C)^+$ *and* $(R_1R_2R_3C)^-$

R_1	R_2	R_3	Net C_{tr} Charge in $(R_1R_2R_3C_{tr})^+$	Net H Charge in $(R_1R_2R_3C_{tr})^+$	Net C_{te} Charge in $(R_1R_2R_3C_{te})^+$	Net C_{te} Charge in $(R_1R_2R_3C_{te})^-$
H	H	H	+0.2348	+0.2551	+0.3068	−0.4335
H	H	Me	+0.1985	+0.2351	+0.2752	−0.3897
H	Me	Me	+0.1690	+0.2191	+0.2504	−0.3544
Me	Me	Me	+0.1444	—	+0.2303	−0.3251
Et	Et	Et	+0.1413	—	+0.2279	−0.3143

In all the species $(R_1 R_2 R_3 C)^+$ considered, the net charge on the central carbon is substantially less than +1 electron, and somewhat less than the charge calculated by the extended Hückel method [*12*]. The net charges of the hydrogen atoms directly bonded to the central carbon also decrease as the extent of substitution of Me for H increases, (column 5, Tab. 8), the hydrogen charges in the central carbon series decrease in a similar fashion.

A comparison of the central atom net positive charge in the species $(Me_3C)^+$ and $(Et_3C)^+$ (rows 4 and 5, Tab. 8) indicate that substitution of hydrogen by methyl groups at the β carbon is much less effective (3%) in reducing the central atom net charge compared to this substitution at the central carbon itself.

In all the ions considered, trigonally hybridized bonds from the central carbon are more effective in reducing the net carbon positive charge than are tetrahedrally hybridized bonds. This effect (along with hyperconjugation requirements, etc.) probably contributes to the preferred planar geometry of the real positive ions.

Although the bond electronegativity equalization method is not suited to calculations of total molecular energy, the atom energy versus net atom charge density curves of Hinze et al. [*9*] used in the equalization method may be employed to analyze the relation between net charge and molecular energy. Figs. 1, 3 and 4 of reference [*9*] indicate that, in general, the energy required to produce an additional partial positive charge $+q$ on an atom increases as the original positive charge of the atom increases. It should be more favourable to the total molecular energy, then, to spread the positive charge over as many atoms as possible.

According to this analysis, the experimental trend of increasing carbonium ion stability is in accord with the trend of calculated central atom net positive charge.

The variability of alkyl group electronegativities predicts not only an increased "delocalization" of the net positive charge in carbonium ions relative to $(CH_3)^+$, but also increased delocalization of the unit negative charge in aliphatic carbanions $(R_1 R_2 R_3 C)^-$. The central (tetrahedrally hybridized) carbon atom net negative charges for the carbanion system are listed in column 7 of Tab. 8. In these species, a lone pair of electrons has been localized in one central carbon (sp^3) atomic orbital, and the orbital charge densities computed from the electronegativity equalization restrictions. Due to the low electronegativity of the central carbon te orbitals here, $\chi^{(1)}_{CH_3} \gg \chi^{(1)}_{H}$ (see Fig. 6) and successive replacement of the hydrogen atoms in $(CH_3)^-$ by alkyl groups leads to increasing delocalization of the unit negative charge.

The calculated effects of alkyl radicals to inductively increase the delocalization of both formal positive and negative charges is due to the peculiar ability of $\chi^{(1)}_{alkyl}$ to be less or greater than $\chi^{(1)}_{H}$, and the conclusions reached above applying to delocalization of charge will not necessarily apply to radicals or atoms whose electronegativity curves do not cross as those in Figs. 5 and 6.

Conclusions

Several remarks concerning the implications of the calculated inductive effects should be made at this point. In the sections concerned with alkanes and the σ bonds of neutral unsaturated hydrocarbons, alkyl groups have been found to exert only very small inductive effects on the ground-state charge distributions. Much larger inductive effects accompanying alkyl substitution have been found for charged species, and for heteroatom derivatives of the hydrocarbons [*28*]. These results tend to confirm the view of INGOLD [*15*] that alkyl groups exhibit polar effects only when influenced by polar groups. The inductive effects of alkyl groups in various saturated hydrocarbon derivatives will be reported in the near future.

The charge distributions for the alkanes reported herein confirm the general view that the C–H and C–C bonds in such molecules are very nearly covalent, and the small C–H bond ionic characters that do exist are in the sense $C^{\delta-} H^{\delta+}$. The continuous but small variations in the net atom charge densities in these molecules display semiquantitative correlations with the corresponding N.M.R. chemical shift variations.

Acknowledgements. The authors wish to thank Mr. M. KAPLANSKY and Mr. J. SICHEL for helpful discussions, and the McGill University Computer Center for programming assistance and machine time. This research was supported by the National Research Council of Canada, and one of us (N.C.B.) also thanks N.R.C. for the award of three scholarships (1963—66). The authors are indebted to the referee for helpful suggestions.

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